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CHLORINATION OF THIOSALT-CONTAINING EFFLUENTS

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CHLORINATION OF THIOSALT-CONTAINING EFFLUENTS

by

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ABSTRACT

Laboratory tests indicate that thiosulphate is oxidized by hypochlorite (the active chlorination species in alkaline or weakly acidic solutions) in at least two discrete stages. At high pH and at room temperature, the reaction appears to stop at the trithionate stage. The further oxidation to sulphate is, however, autocatalysed by the acid generated, so that the reaction is rapidly completed if the pH is allowed to drop freely.

Practical process parameters for the controlled chlorination of a thiosalt-containing mill effluent were determined. At ambient temperatures, a retention time of 30 min would be adequate for a continuous process controlled at pH $\leq$6. For typical plant effluents, about 6 mol Cl_2 and 5 mol $Ca(OH)_2$ are required per mol of S_2O_3 equivalent. Despite the increased reagent requirements, total reagent costs are less than 50% of those calculated for oxidation of hydrogen peroxide. Chlorination, however, introduces a few other potential pollutants which may require additional effluent treatment steps.

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CHLORINATION DES EFFLUENTS CONTENANT DES THIOSELS

par

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RÉSUMÉ

Des essais en laboratoire démontrent que les hyposulfites sont oxydés par l'hypochlorite (les espèces actives de chlorination dans les solutions alcalines ou à faible indice d'acide) en au moins deux phases discontinues. Quand la réaction atteint un pH élevé à la température ambiante, elle semble s'arrêter à la phase trithionate. L'oxydation du sulphate est cependant autocatalysée par l'acide produit. Par conséquent, la réaction se termine rapidement si le pH décroît librement.

On a établi des paramètres pratiques pour contrôler la chlorination des effluents d'usine contenant des thiosels. À la température ambiante, un délai de retention de 30 min suffirait à assurer la continuité du processus à un pH de ≤ 6. En ce qui concerne les effluents typiques d'usine, environ 6 mol Cl_2 et 5 mol $Ca(OH)_2$ sont requis par mol S_2O_3 ou l'équivalent. Malgré le besoin accru de réactifs, le coût global qu'ils entraînent est de 50 % inférieur aux coûts prévus pour l'oxydation du peroxyde d'hydrogène. Cependant, en raison de la chlorination, quelques autres polluants peuvent se manifester et des mesures additionnelles visant l'épuration des eaux usées peuvent s'avérér nécessaires.

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INTRODUCTION

Chlorine is one of the least expensive chemical oxidants available for the destruction of thiosalts in milling effluents (1-3). CANMET has evaluated several other potential processes (4-7), and detailed test reports on a few wet chemical treatment methods are available (8-13). The purpose of the present study was to determine process parameters for the chlorine oxidation of thiosalts as a basis for comparison to other treatment options currently being evaluated under CANMET contract.

To avoid complications of gas handling, tests were conducted with a dilute sodium hypochlorite solution. Hypochlorite is the active oxidizing agent in weakly acidic to alkaline chlorinated solutions:

$$4X) \quad Cl_2 + H_2O = Cl^- + ClO^- + 2H^+ \qquad (1)$$

$$4ClO^- + S_2O_3^{2-} + H_2O = 2SO_4^{2-} + 4Cl^- + 2H^+ \qquad (2)$$

The overall reaction requires 4 mol ClO^- (formed by 4 mol Cl_2) and 10 equivalents OH^- for the complete oxidation and neutralization of one mole of thiosulphate. Preliminary chlorination tests by Rolia and Barbeau (8) indicated mass transfer control in a sparged reactor. The chlorine flowrate determined the length of the induction period and the subsequent rate of oxidation. The results established an overall consumption of 4 mol Cl_2 per mol of thiosalt (S_2O_3 equivalent).

Hypochlorite oxidation tests by Yokosuka et al. (14) indicated that several reactions occur when the pH is allowed to drift freely; e.g.:

$$2S_2O_3^{2-} + ClO^- + H_2O = S_4O_6^{2-} + Cl^- + 2OH^- \qquad (3)$$

$$S_4O_6^{2-} + 3ClO^- + H_2O = S_3O_6^{2-} + SO_4^{2-} + 3Cl^- + 2H^+ \qquad (4)$$

$$S_3O_6^{2-} + 4ClO^- + 2H_2O = 3SO_4^{2-} + 4Cl^- + 4H^+ \qquad (5)$$

The individual thiosalt species can also disproportionate or be oxidized directly to sulphate, complicating the mechanistic interpretation of the test results. Tetrathionate appeared to be quite stable at the low final pH conditions in those tests.

EXPERIMENTAL

Reagents were commercial products of high purity, including standardized stock solutions. About 10 mmol of sodium thiosulphate pentahydrate (MW = 248.2) were dissolved in 800 mL deionized water in a magnetically stirred 1 L open beaker. Solutions of sodium hypochlorite (pH 9, 0.575 N) and 1 N sodium hydroxide were added from burettes, and the pH of the reaction mixture was automatically controlled. All tests were conducted at room temperature.

Two samples were withdrawn at timed intervals. One was quenched into an acidified KI solution for iodometric determination of excess hypochlorite or thiosulphate. The other was diluted with deionized water and saved for total thiosalt analysis by standard $HgCl_2$ acidimetry (1). Table 1 shows the various stoichiometric relationships for the different processes.

Table 1. Stoichiometric equivalents per mol

Species	Standard Iodometry	$HgCl_2^-$ Acidimetry	Complete Oxidation
$S_2O_3^{2-}$	1	2	8
$S_3O_6^{2-}$	-	4	8
$S_4O_6^{2-}$	-	4	14
ClO^-	2	n.a.	2

Differences between the thiosulphate and hypochlorite levels in the samples are determined according to:

$$ClO^- + 2I^- + 2H^+ = Cl^- + I_2 + H_2O \quad (6)$$

$$2S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2I^- \quad (7)$$

The formation of iodate can be prevented by the addition of dilute H_2SO_4 instead of the acetate buffer normally used. A starch indicator was added near the end point, and the titrants were 0.004 N iodine and 0.01 N thiosulphate solutions. Ferric ions interfere, but were not present in the synthetic solutions and were largely precipitated in tests using actual plant effluents.

Excess hypochlorite would interfere with the $HgCl_2$ acidimetry due to its strong oxidizing potential. The samples were left for a sufficient time for all the hypochlorite to react. The total thiosalt content at the sampling time could not be estimated from the acid generated during this period. Titrations were performed using a Metrohm automatic titrator and a 0.01 N NaOH solution.

The experimental setup would be improved by the use of automatic sampling, analysing and recording systems. In the present case, many important parameters were less well defined due to manual operations. All calculations were corrected for volume changes caused by sampling and reagent additions; pipette rinse solutions were returned to the reaction mixture.

RESULTS AND DISCUSSION

PRELIMINARY TESTS

To simplify analysis, batch tests were conducted with nearly equivalent amounts of reagents (13). Initially, all the hypochlorite (~40 mmol) was added at the start. The alkalinity immediately increased to about pH 11, but within 5 min a sharp drop to pH $\leq$2 was observed. The automatic NaOH dispenser could not meet this sudden demand, and the overall reaction was completed at low pH within 10 min. Right after the start, about 22 mol excess NaClO remained in solution, and no intermediate samples could be obtained due to unstable conditions during the course of the tests. Traces of H_2S and elemental sulphur were observed. The solutions were ultimately adjusted to the original pH 10 but only after essentially complete thiosalt oxidation had occurred. The results after different equilibration and adjustment times are presented in Table 2, and indicate reagent requirements of about 4 mol ClO^- and 2 mol OH^- per mol of thiosulphate.

Table 2. Preliminary batch tests started and ended at pH 10

Time	Reagents (mmol)			Residuals (mmol)		
min.	$Na_2S_2O_3$	NaClO	NaOH	$S_2O_3^{2-}$	ClO	$S_xO_6^{2-}$
8	10.5	38.81	18.8	0.33	0	n.a.
13	10.4	38.81	17.6	0.26	0	0.47
20	10.5	40.25	18.5	0	0.5	n.a.

The observations indicate that the reaction occurs in at least two distinct stages, and that the pH is difficult to control in the batch mode. The first stage was marked by a slight rise in pH, followed by an exponential

drop in pH after 3 to 5 min. Such a behaviour would be consistent with oxidation to trithionate according to an earlier postulated mechanism (13) consisting of equation (3) accompanied by:

$$S_2O_3^{2-} + 2ClO^- + H_2O = 2SO_3^{2-} + 2Cl^- + 2H^+ \quad (8)$$

$$S_4O_6^{2-} + SO_3^{2-} = S_2O_3^{2-} + S_3O_6^{2-} \quad (9)$$

The acid generated in equation (8) would moderate the increase in pH predicted by equation (3).

The disappearance of all the thiosulphate marks the beginning of the second step. As postulated previously (13), trithionate is quite stable at moderately high pH and reacts very slowly according to equation (5), generating free acid, SO_4^{2-} and possibly SO_3^{2-} as a reactive intermediate. The free acid apparently catalyses the reaction, since the pH drops exponentially to very low values (ending with a drop of 8 pH units in <30 sec). Traces of H_2S and S^o detected during this period are likely due to unstudied side reactions.

CONTINUOUS OXIDATION TESTS

Next, a series of tests was conducted under more controlled conditions in which the NaClO reagent was slowly added from a 50 mL burette. Test results are plotted as a function of time in Figures 1 to 3 which show the reagent addition rates, the pH profiles, and the titration results for each test. The latter, as stated above, are a measure of the differences between the hypochlorite and thiosulphate or polythionate levels in solution.

Figure 1 shows that most of the thiosulphate (∿10 mmol) disappeared within 5 min, after about 15 mmol hypochlorite had been added. At 15 min, more hypochlorite was added and this reacted fairly slowly until a steep drop in pH occurred at 23 min. By controlling the pH at 6, further

hypochlorite additions reacted very quickly, and the thiosalt level decreased to zero after the stoichiometric amount of NaClO (40 mmol) was added.

The first stage behaviour of the reaction was confirmed in a second test using a more continuous NaClO addition rate, as shown in Figure 2. Again most of the thiosulphate disappeared after addition of about 15 mmol hypochlorite, and the steep pH drop occurred at 15 min. Control at pH 8 was quite difficult because the further reaction would accelerate (autocatalysis) as indicated by the oscillating pH curve. Excess ClO^- levels remained low, but the removal of thiosalts was somewhat incomplete.

A slower first stage NaClO addition rate resulted in the disappearance of the sharp pH drop, as shown in Figure 3 (note the different time scales). Control at pH 10 resulted in the buildup of a large excess of ClO^- because of the inhibition of the second stage. The low residual thiosalt levels indicate that the reaction will still proceed once the pH control is removed (autocatalysis), since significant amounts of acid were generated during the waiting period of several hours before analysis.

The test results including individual titration values, are also summarized in Table 3. Thiosulphate ($S_2O_3^{2-}$) and hypochlorite values were obtained by titration of the KI quenched samples with 0.004 N I_2 and 0.01 N $Na_2S_2O_3$, respectively. Total thiosalts ($S_xO_6^{2-}$) include thiosulphate; hence, the residual thiosalt levels plotted in Figures 1 to 3 were taken to be $[S_xO_6^{2-}] - \frac{1}{2}[S_2O_3^{2-}]$ during the first stage of the reaction. If further oxidation to sulphate is negligible during this period at pH $\geq$10, the following relationship should hold (S balance):

$$[S_2O_3^{2-}]_0 = [S_2O_3^{2-}] + \tfrac{1}{2}x([S_xO_6^{2-}] - \tfrac{1}{2}[S_2O_3^{2-}]) \qquad (10)$$

The values listed in Table 3 yield x $\sim$5, indicating that the first stage oxidation product cannot be trithionate alone.

The last column of Table 3 indicates the amount of acid which would be generated if all reagent additions were stopped at that particular time. These values do not yield reliable estimates of the actual amounts of thiosalts remaining at a given time. Instead, the excess ClO^- levels and equation (5) were used to estimate the $S_xO_6^{2-}$ ranges shown in Figure 4 which combines the results of all three tests. The first stage, corresponding to the linear disappearance of thiosulphate at high pH, was found to be highly reproducible. The second stage disappearance of the thiosalts was faster and more complete at the lower pH values. Considerations of NaClO addition rates and pH response times during the test at pH 6, indicated that a 15 min retention time would be adequate for the continuous oxidation of synthetic effluents. The observed reagent requirements for the complete oxidation and neutralization of synthetic thiosulphate solutions were close to the values predicted from equations (1) and (2).

Tests with Real Milling Effluents

Further testwork was conducted on samples of actual mill effluents received from the Brunswick Mining and Smelting (BMS) plant near Bathurst, New Brunswick. Although the pH and thiosalt contents of these samples were found to be dependent on the sampling and storage history, they provided a fairly typical background matrix as shown in Table 4. The thickener overflow sample contained appreciably higher amounts of iron (mostly ferrous), lead, manganese and zinc; precipitates generally formed above pH 4.

The test results in Table 5 indicate that hypochlorite consumptions for real effluents increased to about 1.5 times the requirements anticipated based on the oxidation of synthetic solutions. This behaviour was not observed with H_2O_2 oxidants (12,13). Furthermore, it is not due to ordinary

reducing agents; e.g., Fe^{2+}, and, indeed, the prior removal of iron in some of the tests did not significantly alter the NaClO requirements. Therefore, it is suspected that some of the matrix ions or organics might form adducts with ClO^- or Cl_2 that could be responsible for the odour generating problems frequently mentioned in the literature (3,14) and also observed in these tests. The generation of both high chloride levels in solution (~4 g/L) and possible toxic chloro-organics would further deter the application of the chlorination process for industrial milling effluents.

For the treatment of an effluent containing 1000 mg/L S_2O_3 at a flow-rate of 10,000 L/min, and estimated costs of \$135/T Cl_2 and \$42.50/T $Ca(OH)_2$, the following annual reagent costs are obtained.

S_2O_3 output = 10 kg/min = 5,781.6 T/Y	= 46.93 Mmol/Y
Cl_2 required = 281.6 Mmol/Y = 22,000 T/Y	= \$ 3.0 M/Y
Lime required = 234.6 Mmol/Y = 19,000 T/Y	= \$ 0.8 M/Y
Total reagent costs	\$ 3.8 M/Y

CONCLUSIONS

Test results basically confirm the postulated reaction mechanism for the oxidation of thiosalts by hypochlorite (13) in which thiosulphate at moderate pH is first oxidized to trithionate via a combination of equations (3), (8) and (9). Depending on the relative rates of reactions (3) and (8), the overall first stage reaction could approximate either of the following equations:

$$3S_2O_3^{2-} + 4ClO^- + H_2O = 2S_3O_6^{2-} + 4Cl^- + 2OH^- \quad (11)$$

$$2S_2O_3^{2-} + 4ClO^- = S_3O_6^{2-} + SO_4^{2-} + 4Cl^- \quad (12)$$

This would agree with the observed hypochlorite consumption during the first stage (~1.5 mol/mol $S_2O_3^{2-}$), the moderate pH increase, and the following thiosalt relationship from equation (10):

$$2[S_2O_3^{2-}]_0 = 2[S_2O_3^{2-}] + 3([S_3O_6^{2-}] - \tfrac{1}{2}[S_2O_3^{2-}]) + \Delta SO_4^{2-} \qquad (13)$$

The second stage oxidation of trithionate to sulphate occurs very slowly above pH 7 but is catalysed by the acid generated in the reaction according to equation (5). For practical purposes, control of this second stage at pH 6 seems to optimize reagent requirements and reaction times, and minimizes the byproduction of H_2S and S^o. Overall reagent requirements for the chlorination of industrial solutions appear to be 6 mol Cl_2 and 5 mol lime per mol of thiosulphate equivalent. Considering the average NaClO flow rate of 2 mmol/min to oxidize 10 mmol thiosulphate in a reliable and well controlled manner, a retention time of 30 min is indicated for industrial solutions with thiosalt concentrations similar to those given in Table 4.

The estimated reagent costs of $3.8 M/Y compare favourably with reagent costs of $8.5 M/Y for the oxidation of similar solutions by hydrogen peroxide (12), but the chlorine oxidation process would also generate up to 4 g/L additional Cl^- in solution as well as possible chloro-organics and odour causing adducts.

ACKNOWLEDGEMENTS

Instrumental and analytical assistance from E. Rolia and G.A. Hunt are gratefully acknowledged.

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Table 3. Data for the controlled NaClO addition tests presented in Figures 1-3.

Time	Reagents (mmol)			Titrated (mmol)			
min	NaClO	NaOH	pH	$S_2O_3^{2-}$	ClO^-	$S_xO_6^{2-}$	ΔH^+
0	0	0	6.0	10.3	-	4.9	-
5	14.4	0	10.9	1.1	-	4.0	-
19	21.6	0	10.2	-	4.9	2.8	1.0
31	28.8	7.2	6.0	-	-	1.5	-
41	34.5	11.4	6.0	-	-	0.5	-
44	35.9	12.3	6.0	-	-	0.3	-
50	38.8	13.5	6.0	-	-	-	-
0	0	0	5.4	10.7	-	4.8	n.a.
3	10.1	0	10.9	3.8	-	4.6	n.a.
10	20.1	0	10.4	-	2.85	3.3	n.a.
15	28.8	0	9.8	-	4.85	2.0	n.a.
23	30.5	7.2	6.5-8.5	-	0.31	1.6	n.a.
34	37.7	12.5	6.8-8.2	-	0.05	0.8	n.a.
42	38.2	12.5	7.2	-	-	n.a.	n.a.
0	0	0	10.0	10.4	-	4.8	-
5	5.8	0	10.9	6.5	-	4.5	-
17	14.4	0	10.8	1.0	-	4.1	-
34	28.8	1	10.0	-	4.2	1.6	4.3
44	28.8	4.7	10.0	-	3.4	1.6	0.97
48	34.5	5.5	10.0	-	22.5	0.8	3.2
58	34.5	7.2	10.0	-	19.7	n.a.	n.a.
65	37.4	8.5	10.0	-	21.7	0.3	2.66
98	37.4	10.0	10.0	-	8.7	0.2	-

Table 4. BMS effluent compositions

BMS Stream Descriptions		Tailings Influent Received 7/83	Tailings Influent Average 1983*	Thickener O/F Received 7/84	Thickener O/F Average 1983*
mg/L	Ca	540	393	540	928
	Cl	130	n.a.	140	n.a.
	Cu	<0.1	0.5	1	2.6
	Fe	0.3	3.7	380	45
	Pb	0.1	7.8	3	27.7
	Mg	35	6.5	48	46.9
	Mn	7	n.a.	34	n.a.
	Na	710	649	390	229
	S_T	1150	(925)	1550	(1419)
	$S(SO_4)$	930	547	1060	834
	Zn	10	6.4	210	137

* Data obtained from the Noranda Research Centre (2)

Table 5. Oxidation of BMS effluents

Time min	Reagents (mmol)			pH	Mol Ratios/S_xO_6	
	NaClO	NaOH	S_xO_6		ClO^-	OH^-
0	0	0	3.3	2.3	n.a.	-
7	1.8	9	n.a.	3.5	n.a.	n.a.
17	14.4	18	2.07	3.2	11.7	14.6
20	18.4	19	1.86	3.0	12.8	13.2
25	23.6	20	1.36	2.8	12.2	10.3
35*	35.1	26.6	0.11	6.1	11.0	8.3
0	0	0	0.89	6	n.a.	-
3	4.03	2.5	0.63	6	15.5	9.6
7	5.75	3.9	0.42	6	12.2	8.3
12	7.13	4.0	0.28	6	11.7	6.6
0*	0	0	2.78	6.3	n.a.	-
6	6.62	0.3	2.19	6	11.2	0.51
17	15.8	2.7	1.57	6	13.1	2.23
27	19.5	4.3	1.04	6	11.2	2.47
40	25.3	6.2	0.46	6	10.9	2.67
52	27.4	6.8	0.20	6	10.6	2.93
102	28.0	6.8	0.15	6	10.6	2.59
137	29.6	6.8	0	6	10.6	2.45

* After preoxidation and removal of iron precipitate

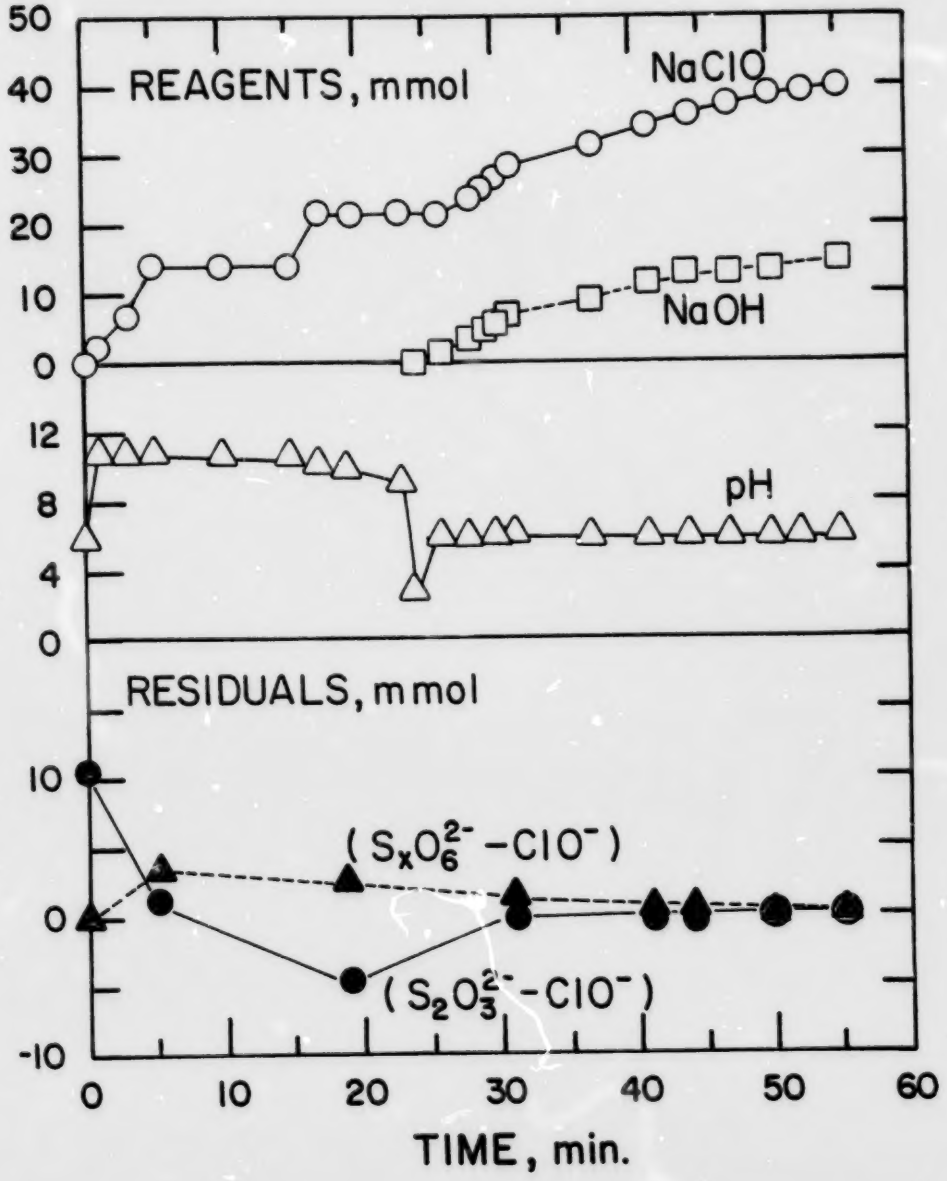

Figure 1. Thiosulphate oxidation, second stage controlled at pH 6.

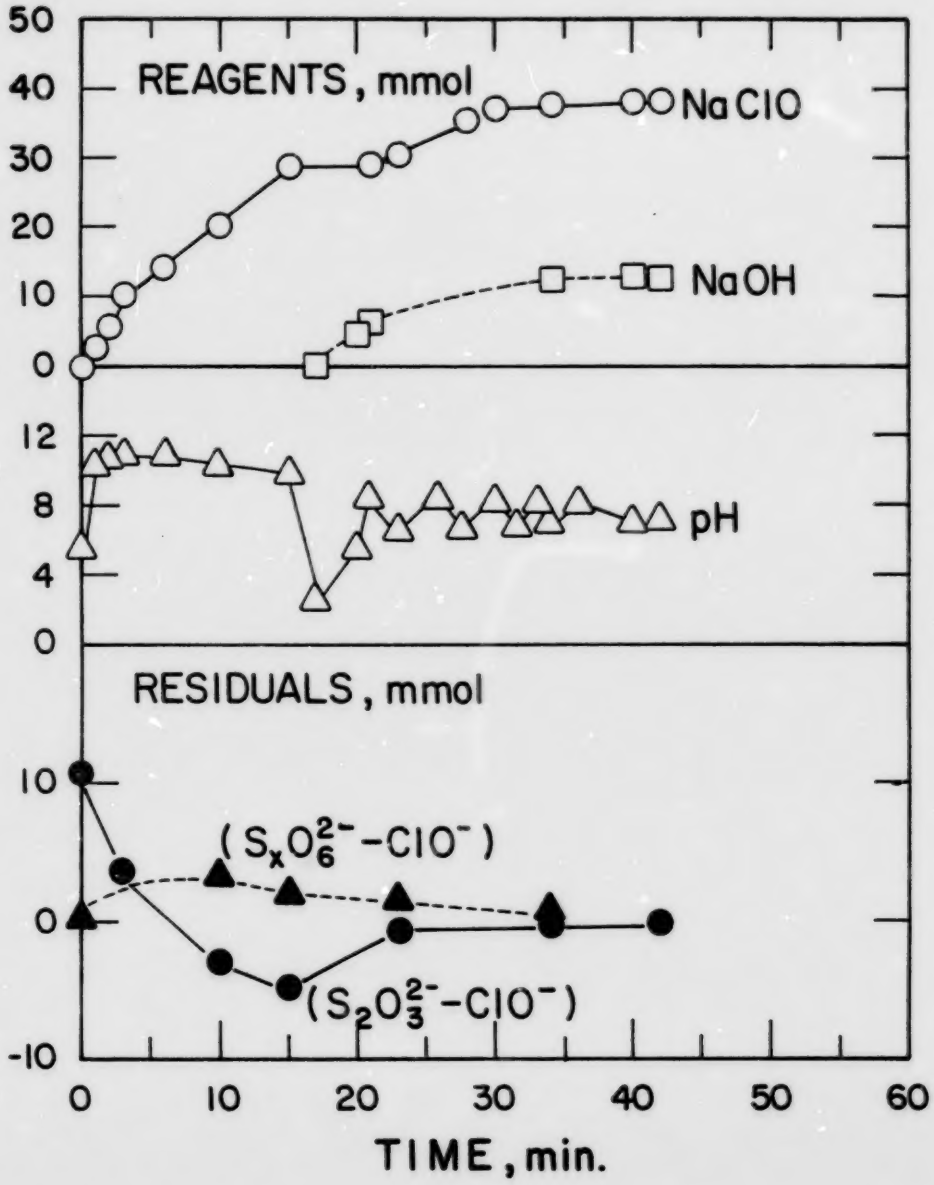

Figure 2. Thiosulphate oxidation, second stage controlled at pH 8.

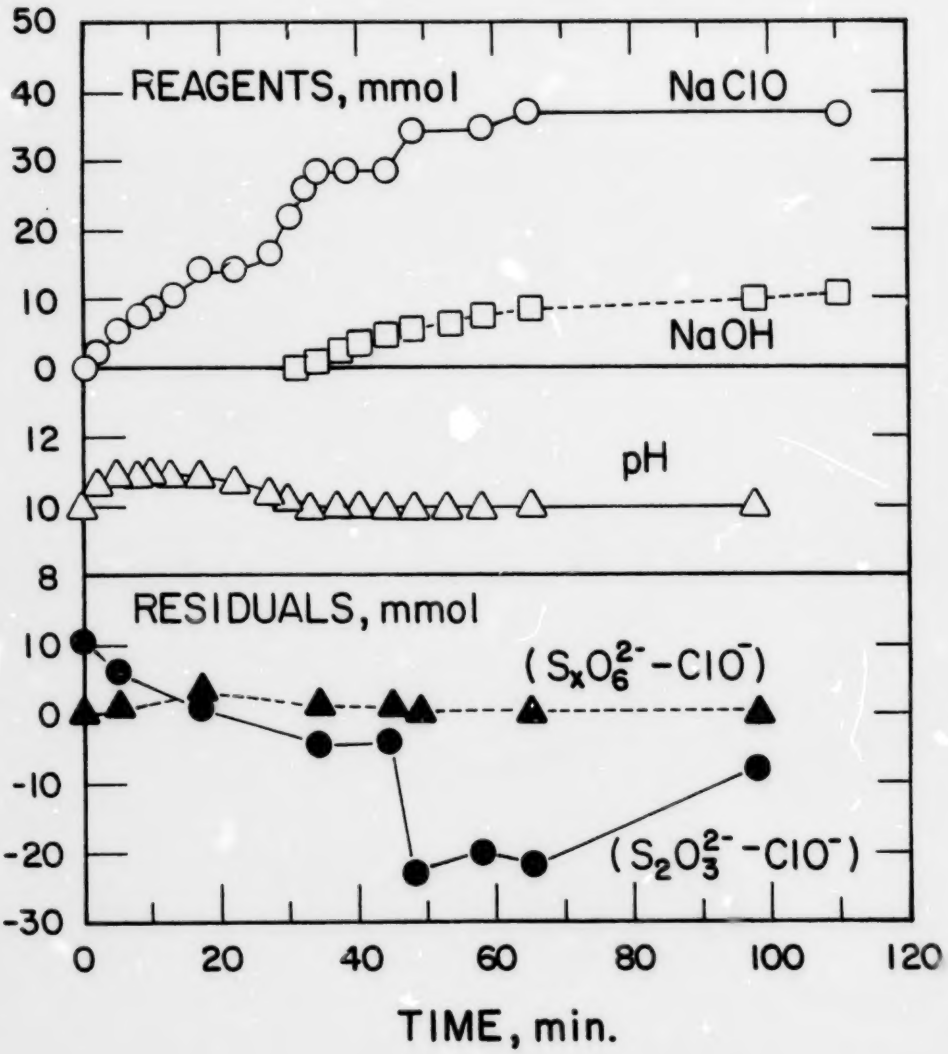

Figure 3. Thiosulphate oxidation, second stage controlled at pH 10.

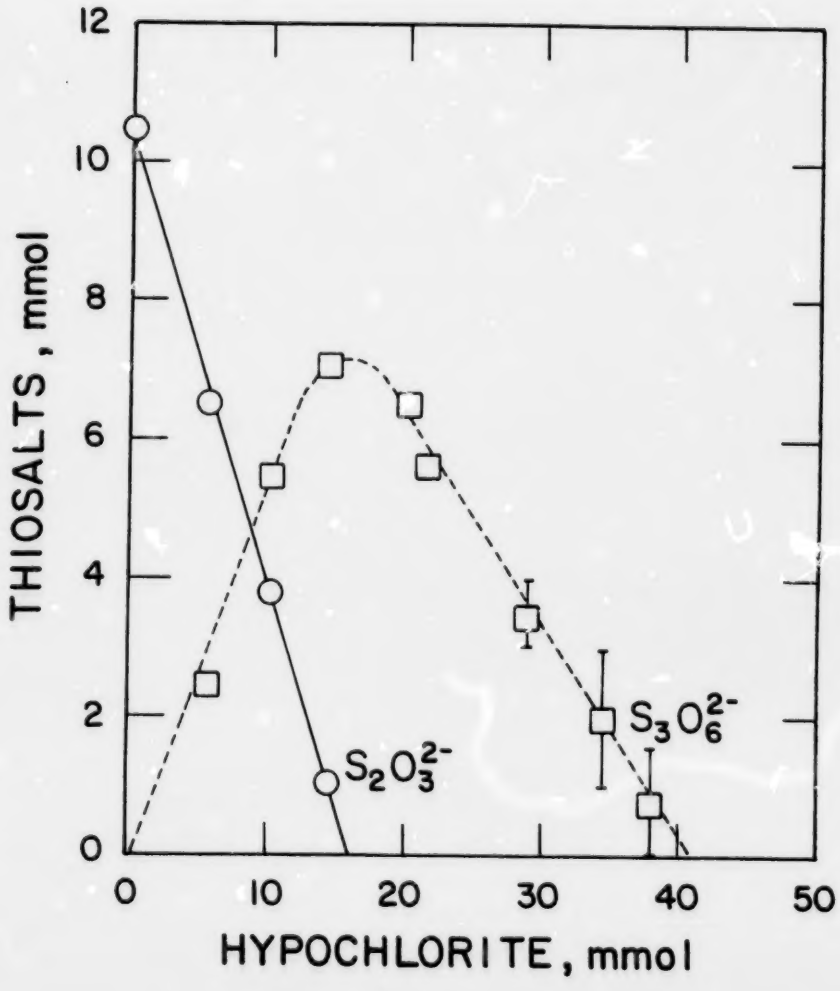

Figure 4. Thiosulphate oxidation, composite results.